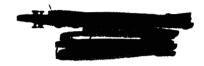
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APPLICATION OF THE MULTI-CONFIGURATION APPROXIMATION TO THE DETERMINATION OF THE DIPOLE FORCE FOR ATOMS OF THE BERYLLIUM AND BORON TYPES

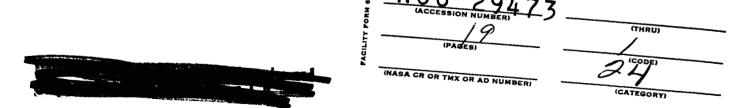
by

A. B. Bolotin and A. P. Yutsis

Translation of "Primeneniye mnogokonfiguratsionnogo priblizheniya pri opredelenii sily dipolya dlya atomov tipa berilliya i bora" Zhurnal Eksperimental'noy i Teoreticheskoy Fiziki, Vol. 24, 537-544, 1953

GPO PRICE \$_	
CFSTI PRICE(S) \$_	
Hard copy (HC) _	\$ 1,00
Microfiche (MF)	,50
ff 653 July 65	

NATIONAL AFRONAUTICS AND SPACE ADMINISTRATION WASHINGTON June 1963



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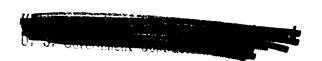
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Expressions are presented for the total dipole force for 1s²2s2p--1s²2s² transitions of atoms of the beryllium type and 1s²2s2p²--1s²2s²2p transitions of atoms of the boron type in a two-configuration approximation. The constants of the analytic single-electron wave functions are determined for the atoms B, C⁺, N⁺⁺, 0⁺³ and F⁺⁴ in the 1s²2p³ and 1s²2s2p² configurations. The analytic single-electron wave functions are used to determine values of the total dipole force, the oscillator strength, and the transition probability for 1s²2s2p--1s²2s² transitions of the atoms Be, B⁺, C⁺⁺, N⁺³ and 0⁺⁴ and for 1s²2s2p²--1s²2s²2p transi-

tions for the atoms B, C^+ , N^{++} , O^{+3} and F^{+4} .



In [1, 2] it was shown that the multi-configuration approximation [3] is a considerable refinement on the quantum-mechanical method of atomic calculation in connection with computations of the total energy of the atom. Accordingly, it would appear reasonable to apply this approximation to the determination of various other physical quantities. The present article is concerned with the use of the multi-configuration approximation in determining the quantities that play a part in the transition theory for atoms of the beryllium and boron types.

In [2] Yutsis and Kavetskis showed that for the fundamental configuration of atoms of the beryllium type the multi-configuration approximation actually reduces to the two-configuration ap-

proximation 1s 2s --1s 2p . The approach outlined in section 2 of [2] leads to the conclusion that in the case of the fundamental configuration of atoms of the boron type it is possible to confine

oneself to the two-configuration approximation $1s^22s^22p-1s^22p^3$.

By virtue of the same reasoning, in the case of the 1s2s2p

configuration of atoms of the beryllium type and the 1s 2s2p configuration of atoms of the boron type it is possible to confine oneself to a single-configuration approximation, since in these circumstances there are no configurations of great weight [3] relative to the given configurations. Accordingly, in this article we shall use a two-configuration approximation for the fundamental configurations of atoms of the beryllium and boron types, and a single-configuration approximation for the excited configurations

 $1s^{2}2s2p$ and $1s^{2}2s2p^{2}$.

We shall base the numerical calculations on analytic singleelectron wave functions of the type defined in [4], since one of the authors has already determined the constants of functions of this type for certain relevant configurations [1]. We have since determined these constants for the 1s22p3 and 1s22s2p2 configura-

tions of the atoms B, C^+ , N^{++} , 0^{+3} and F^{+4} .

In [2] a two-configuration approximation was applied to atoms of the beryllium type using hydrogen-like analytic single-electron wave functions [5]. In view of the fact that analytic functions of another type are used here, we present the results of determining the energy corrections for a two-configuration approximation both for atoms of the boron type and for atoms of the beryllium /538 type. These results are necessary in order to obtain the overall wave function in the two-configuration approximation, this being needed to determine the total dipole force in the same approximation.

2. EXPRESSION FOR TOTAL DIPOLE FORCE

In the theory of electric dipole radiation an important part is played by an intermediate quantity which in the case of an LS coupling is determined as follows:

$$S(LS, L'S) = S(L'S, LS) = \sum_{M_LM_L, M_S} S(LSM_LM_S, L'SM_L, M_S)$$
.
(2.1)

Henceforth we shall refer to this quantity as the total dipole force, since it represents the sum of the dipole forces between the individual states of corresponding terms. The dipole force is determined as follows:

$$S(LSM_LM_S, L'SM_LM_S) = \left| \int \Psi^*(LSM_LM_S | X)P\Psi(L'SM_LM_S | X) dX \right|^2.$$
(2.2)

In (2.1) and (2.2) L, S, M_L and M_S are quantum numbers of the whole atom, L and S characterizing the term. In (2.2) P is the operator of the electric dipole moment, X denotes all the coordinates of all the electrons, while the integral sign in (2.2) denotes integration with respect to all the spatial and summation with respect to the spin coordinates of all the electrons.

We shall consider transitions between the configurations 2 $^{q+1}$ (below we denote this by 3) and 2 2 2 2 q (denoted by 1). When q=0 we have the case of atoms of the beryllium type, and when q=1 the case of atoms of the boron type. For electric dipole radiation in the case of atoms of the beryllium type we get 1 P $^-$ S transitions, and in the case of atoms of the boron type

²S, ²P, ²D - ²P transitions; in this notation the term of configuration 3 occupies the first place and that of configuration 1 the second. As already pointed out, in the case of an excited configuration 3 we shall confine ourselves to a single-configuration approximation, while for the fundamental configuration 1 we shall use the two-configuration approximation 1-2, where 2 denotes the

configuration $1s^22p^{q+2}$. Then the overall wave function for configuration 1 in accordance with equation (2.9) of [3] can be written in the form:

$$\Psi(A_1|X) = \frac{1}{\sqrt{1+a_{12}^2}} \left[\Psi(A_1|X) + a_{12} \Psi(A_2|X) \right], \qquad (2.3)$$

Here Ψ (A₁|X) and Ψ (A₂|X) are the overall wave functions for

configurations 1 and 2 in the single-configuration approximation. a is a constant, the absolute value of which, as proposed in [3], 12

will be called the "weight" of configuration 2 relative to configuration 1.

We shall express the overall wave functions for the different configurations in the single-configuration approximation as linear combinations of determinants, composed of single-electron wave functions, which we shall consider orthonormalized. It is possible to assume [6] that the single-electron wave functions of the 1s-electrons are the same in all three configurations of a given atom. Then for the total dipole force we obtain the following expressions:

$$S(1.3) = \frac{2}{1+a^{2}} \left[N(r2s, 2p)_{13} N(2s, 2s)_{13} - \frac{a_{12}}{\sqrt{3}} N(r2s, 2p)_{32} N(2p, 2p_{32}) \right]$$

$$(2.4a) \frac{\sqrt{539}}{12}$$

for the $1s^2 2s2p$ $^1P - 1s^2 2s^2$ S transition of atoms of the beryllium type and

$$S(1.3) = \frac{2a}{3(1 + a^2)} \times$$

$$X \left[N(r2s, 2p)_{13}N(2s, 2s)_{13}N(2p, 2p)_{13} + \frac{a_{12}}{\sqrt{2}}\beta N(r2s, 2p)_{32}N^{2}(2p, 2p)_{32}\right]^{2}$$
(2.4b)

for the 1s 2s2p S, P, D - 1s 2s 2p P transitions of atoms of the boron type, where α and β have the following values:

$${}^{2}S - {}^{2}P + {}^{2}P - {}^{2}P + {}^{2}D - {}^{2}P.$$
 $\alpha = 1 \qquad 9 \qquad 5$
 $\beta = -2 \qquad 1 \qquad 1$

N are radial integrals defined as follows:

$$N(\mathbf{r}^{k}\mathbf{n}, \mathbf{n}', \mathbf{n}')_{ij} = \int_{0}^{\infty} \mathbf{r}^{k} P_{i}(\mathbf{n}, \mathbf{n}, \mathbf{n}', \mathbf{n}', \mathbf{n}') d\mathbf{r}.$$
 (2.5)

Here the radial wave functions P_i (nⁱ|r) and P_j (n'i'|r) relate to configurations i and j respectively. When k=0 the integral (2.5) reduces to N (nⁱ, n'i'), which appears in (2.4) with n'i' = ni.

Substituting $a_{12} = 0$, from (2.4) we obtain the corresponding expressions for the total dipole force in the single-configuration approximation. On the other hand, substituting $a_{12} = 1$, and

neglecting the first term in the square brackets, we get expressions, divided by 2, for the total dipole force, relating to transitions between corresponding terms of configurations 2 and 3 in the single-configuration approximation.

3. VALUES OF THE WAVE FUNCTION CONSTANTS

We shall use analytic single-electron radial wave functions of the following form:

$$P (1s|r) = \sqrt{4\eta \beta_{a} 3} re^{-\eta_{a} r},$$
 (3.1a)

P
$$(2s|r) = \sqrt{4\pi^{5}/3Nr}(re^{-\pi r} + \xi e^{-\pi br}),$$
 (3.1b)

$$P(2p|r) = \sqrt{4\eta^5c^5/3r^2} e^{-\eta cr},$$
 (3.1c)

where

$$\xi = -3 (a + b)^3 / \eta (1 + a)^4$$

and

$$N = 1 + \frac{16\xi\eta}{(1+b)^4} + \frac{\xi^2\eta^2}{3b^3}$$
 (3.3)

These functions satisfy the orthonormalization condition. The constants, η , a, b, and c are determined by seeking a minimum for the total energy of the atom. Values of these constants for configurations 1, 2 and 3 of atoms of the beryllium type and also for configuration 1 of atoms of the boron type are given in [4]. Those for configurations 2 and 3 of atoms of the boron type will be found in Table 1.

For completeness, we give values of these constants for all the terms, although for the solution of our problem it is not essential to know the wave functions of all the terms of the given configurations. The table also includes theoretical and experimental values of the total energy, the latter being taken from [7].

In order to make use of the overall wave function in the two-configuration approximation (2.3) it is necessary to determine the constant a For its determination we have from equations (2.11)

and (2.12) of [3]

$$a_{12} = \Delta E^1 / E_{12},$$
 (3.4)

$$\Delta E^{1} = E_{12}^{2} / (\Delta E^{1} + E_{1} - E_{2}), \qquad (3.5)$$

where

$$\Delta \mathbf{E}^1 = \mathbf{E}^1 - \mathbf{E}_1$$

is the correction to the energy of configuration 1 for the two-configuration approximation, E_1 and E_2 are the energies of configurations 1 and 2 in the single-configuration approximation, and

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E¹ is the energy of configuration 1 in the two-configuration approximation, E is the nondiagonal matrix element connecting configura-

tions 1 and 2. An expression for this element is given in equation (3.7) of [2] for atoms of the beryllium type, for atoms of the boron type the corresponding equation is:

$$E_{12} = (\sqrt{2}/3) G_1(2s, 2p)_{12} N^2(1s, 1s)_{12} N(2p, 2p)_{12}.$$
 (3.7)

Here N is determined in accordance with (2.5) for k = 0, and G_1 is found in exactly the same way as in (3.7) of [2].

Values of the constant a and the correction ΔE^1 are presented in Table 2.

4. NUMERICAL RESULTS

With the aid of the single-electron wave functions (3.1) and values of the constants a_{12} from Table 2, the total dipole force is

determined from equations (2.4). The results are given in Table 3 together with the differences between the energies and values of the integrals N(r2s, 2p). Within the limits of permissible error, the integrals N(n1, n1) are equal to unity.

TABLE 1

Values of the Constants of the Analytic Wave Functions (3.1) for 2 3 2 2

the 1s 2p and 1s 2s2p Configurations of Atoms of the Boron Type (Energies in Atomic Units).

	В	C ₊	N ⁺⁺	0+3	F+4			
		1 s ² 2p 2 _p	3					
a Ma 2Mc ^E theor.	3.65 4.67 2.36 -23.951	3.35 5.66 3.42 -36.458	3.15 6.66 4.44 -51.727	3.02 7.65 5.48 -69.755	2.93 8.64 6.50 -90.539			
E exp.	1	-36.663 \	-51.917	-69.944	-90.725			
a $\eta_{\mathbf{a}}$ $2\eta_{\mathbf{c}}$ $^{\mathbf{E}}$ theor.	3.60 4.67 2.39 -24.002	3.33 5.66 3.45 -36.530	3.13 6.65 4.46 -51.822	3.01 7.65 5.48 -69.871 -70.098	2.91 8.64 6.53 -90.682 -90.909			
exp.	•	4 S)	1 10.070	,01,0,			
a Ma 2Mc theor.	3.55 4.67 2.42 -24.078	3.30 5.66 3.48 -36.641	3.11 6.66 4.49 -51.958	3.00 7.65 5.51 -70.046	2.89 8.64 6.58 -90.884			
$\Xi_{ ext{exp.}}$		-36.786	-52.116	-70.207	-91.048			
	1 s ² 2s2p ² 2 _P							
a Na b Nb	3.62 4.69 3.23 4.18	3.30 5.67 2.88 4.95	3.07 6.66 2.60 5.64	2.89 7.65 2.38 6.30	2.75 8.64 2.21 6.94			

[Table 1 continued]

	В	C+	N++	0+3	F+4				
2Nc 2N Etheor.	2.31 2.59 -24.145	3. 54 3. 44 -36. 727	4. 56 4. 34 -52. 095	5.66 5.29 -70.224	6.78 6.28 -91.099				
E exp.	-24.324	-36.928	-52.302	-70.437	-91.327				
_		$^{2}\mathrm{S}$							
a Ma b Mb 2Mc 2M Etheor.	3.52 4.69 3.13 4.17 2.32 2.66 -24.214	3.19 5.67 2.85 5.06 3.48 3.55 -36.812	3.01 6.66 2.64 5.84 4.51 4.43 -52.188	2.87 7.65 2.49 6.63 5.59 5.40 -70.318	2.81 8.65 2.38 7.33 6.59 6.21 -91.205				
E exp.	-24.365	-36.993	-52.371	-70.512	-91.409				
	2 _D								
a $\mathbb{N}_{\mathbf{a}}$ b $\mathbb{N}_{\mathbf{b}}$ $2\mathbb{N}_{\mathbf{c}}$ $2\mathbb{N}$ Etheor. $\mathbb{E}_{\mathbf{exp}}$.	3.48 4.69 2.97 4.00 2.37 2.70 -24.288	3. 23 5. 68 2. 76 4. 85 3. 48 3. 52 -36. 919	3.03 6.67 2.60 5.72 4.53 4.40 -52.329	2.89 7.66 2.47 6.55 5.62 5.30 -70.498	2.80 8.65 2.38 7.35 6.74 6.18 -91.415				
4 P									
a Ta b Tb 2Nc 2N Etheor. Eexp.	3.53 4.69 2.95 3.92 2.39 2.66 -24.441	3.22 5.68 2.60 4.59 3.55 3.53 -37.129	3.01 6.68 2.41 5.35 4.62 4.44 -52.596	2.85 7.67 2.35 6.32 5.70 5.38 -70.813	2.73 8.65 2.32 7.35 6.78 6.28 -91.785				

TABLE 2

Values of the Constant a $_{12}$ and the Energy Correction in the

Two-Configuration Approximation for the Fundamental Configura-tion of Atoms of the Beryllium and Boron Types (Energies in Atomic Units)

	Ве	B [†]	‡,	N ⁺ 3	0+4
8	0.33	0.31	0.305	0.30	0.30
ΔE ¹	-0.039*	-0.057	-0.073	-0,088	-0.103
	В	t ₀	N++	0+3	F ⁺ 4
ď	-0.24	-0.23	-0.22	-0.22	-0.21
12 0E ¹	-0.0335	-0.042	-0.050	-0.058	990.0-
	`				

* The erroneous value -0.036 is given on page 1143 of [2].

TABLE 3

Values of the Total Dipole Force, Oscillator Strength, and Transition Probability for Atoms of the Beryllium and Boron Types (Transition Probability in Units of 10 sec , All Other Quantities Atomic Units)

		Ве	\mathtt{B}^+	C++	N+3	0+4
		1s ² 2s2p 1	P - 1s ² 2s	2 1 _S		
ΔΕ	$\left\{\begin{array}{c} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{array}\right.$	0.194 0.233 0.192	0.299 0.356 0.332	0.391 0.464 0.464	0.468 0.556 0.594	0.541 0.644 0.723
N(r2s, 2p)		2.85	1.86	1.38	1.08	0.89
N(r2s, 2p)32		2.91	1.84	1.36	1.08	0.89
s(¹ P, ¹ s)	∫a lb	16.2 9.5	6.95 4.30	3.79 2.37	2.35 1.48	1.59
f(¹ P, ¹ S)	{ a b	0.70 0.49	0.46 0.34	0.33 0.24	0.24 0.18	0.19 0.14
w(¹ ₱,¹s	{a {b	8.4 8.6	13.2 13.8	16.0 16.8	17.1 18.2	17.8 18.9
•		В	c ⁺	N ⁺⁺	0+3	F+4
	1s ² 2s2p ²² S - 1s ² 2s ² 2p ² P					
ΔΕ	a { b } c	0.265 0.298 0.290	0.403 0.446 0.440	0.520 0.570 0.597	0.623 0.681 0.750	0.704 0.770 0.901
N(r2s, 2p)		2.13	1.57	1.25	1.03	0.89
$N(r2s, 2p)_{32}$		2.11	1.58	1.26	1.06	0.91
s(2s,2p)	(a lb	3.03 5.11	1.64 2.74	1.04	0.71	0.52

[Table	3	continued]
TADTE)	COHUTHAGA

[Table 3 continu	ued]	3	f	•	İ		
f (² 5, ² P)	{ a } b	0.27 0.51	0.22 0.41	0.18 0.32	0.15 0.26	0.12 0.22	
w (² s̄, ² P)	∫a ∫b	5.97 14.4	11.4 25.9	15.6 33.7	18.2 39.3	19.3 41.9	
	1s ² 2s2p ² ² P - 1s ² 2s ² 2p ² P						
ΔΕ	a {b c	0.333 0.367 0.331	0.488 0.531 0.505	0.613 0.663 0.666	0.716 0.774 0.824	0.810 0.876 0.982	
N(r2s, 2p)		2.14	1.55	1.23	1.02	0.86	
N(r2s, 2p)32		2.14	1.59	1.27	1.06	0.92	
$S(^2P,^2P)$	a { b	27.4 17.8	14.4 9.53	9.12 6.13	6.24 4.18	4.46 2.99	
$f(^2\overline{P},^2P)$	{ a b	1.01 0.72	0.78 0.56	0.62 0.45	0.50 0.36	0.40	
$W(^2\overline{P},^2P)$	{a b	35.9 31.1	59 . 3 50 . 4	74.5 63.3	91.3 68.9	83.9	
		В	C ⁺	N++	0+3	F+4	
•	1s ² 2s2p ² D - 1s ² 2s ² 2p ² P						
ΔE	a { b c	0.190 0.224 0.218	0.296 0.339 0.342	0.379 0.429 0.461	0.442 0.500 0.579	0.494 0.560 0.697	
N(r2s, 2p) ₁₃		2.12	1.57	1.24	1.01	0.87	
N(r2s, 2p) ₃₂		2.11	1.58	1.27	1.06	0.91	

[Table 3 continued]

s (² D, ³ P)	a 14.9	8.19	5.15	3.40	2.52
	b 9.74	5.44	3.48	2.27	1.70
f(2D,2P)	∫a 0.19	0.16	0.13	0.10	0.083
	b 0.14 ₅	0.12	0.10	0.075	0.063
$W(^2\overline{D}, ^2P)$	a 2.18	4. 50	5.97	6.26	6.44
	b 2.32	4. 50	5.86	6.04	6.34

Note: a -- with the aid of the single-configuration approximation, b -- with the aid of the multi-configuration approximation, c -- experimental data.

Table 3 also includes values of the oscillator strength for transitions from the excited state to all states of a term of the fundamental configuration together with the corresponding transition probabilities. The oscillator strength is determined as follows:

$$f(\overline{LS}, L'S) = \frac{2}{3(2L+1)(2S+1)} \Delta ES(LS, L'S) = \frac{2L'+1}{2L+1} f(LS, \overline{L'S})$$
(4.1)

and the transition probability

$$W(\overline{LS},L'S) = \frac{2L'+1}{3(2L+1)(2S+1)} (\Delta E)^{3}S(LS, L'S) = \frac{2L'+1}{2L+1} W(LS,\overline{L'S}).$$
(4.2)

Here ΔE is the difference between the energies of the LS and L'S terms of the corresponding configurations, μ is the fine-structure constant.

Clearly, unlike the total dipole force, the transition probability and the oscillator strength do not possess the property of symmetry, since they are averaged only with respect to the initial, but not the end states.

Equations (2.4), (4.1) and (4.2) are given in atomic units. The same units are used for the quantities in Table 3, except for the transition probability which is given in units of 10 sec. In these units equation (4.2) is written in the approximate form:

$$W(\overline{IS}, L'S) = \frac{213(\Delta E)^3 S(IS, L'S)}{(2L+1)(2S+1)}, \qquad (4.3)$$

where ΔE and S(LS,L'S) are in atomic units, and $W(\overline{LS},\ L'S)$ in units 8 -1 of 10 sec .

For purposes of comparison, Table 3 includes values of the total dipole force, the oscillator strength, and the transition probability obtained with the aid of both the multi-configuration and the single-configuration approximation.

5. CONCLUSIONS

It is clear from Table 2 that the energy correction for the multi-configuration approximation for atoms of the boron type and for atoms of the beryllium type increases in absolute magnitude with increase in the atomic number in the periodic table, this increase being less for atoms of the boron type than for atoms of the beryllium type. Unlike the energy correction, the constant a decreases in absolute magnitude with increase in the atomic

number.

It is clear from Table 3 that the differences between the energies of the excited and fundamental configurations of atoms of the beryllium and boron types, determined with the aid of the multi-configuration approximation, are greater than in the case of the single-configuration approximation. In the case of light atoms they exceed the experimental values, while with increase in atomic number they occupy an intermediate position between the single-configuration and experimental data.

The total dipole force, determined with the aid of the multi-configuration approximation, is 1.5-1.7 times less than the corresponding values determined with the aid of the single-con-

figuration approximation, except for the $^2S-^2P$ transition of atoms of the boron type, where it is as many times greater.

The multi-configuration approximation introduces unimportant

changes into the values of the probability of the ¹P - ¹S transi-

tion in atoms of the beryllium type and of 2P , $^2D - ^2P$ transitions in atoms of the boron type; however, it increases by more than

twice the probability of the $^2S-^2P$ transition in atoms of the boron type. In the first two cases the change in the total dipole force is compensated by the change in the difference between the energies, while in the latter case the effects of both changes are additive owing to the negative signs of the coefficient β in (2.4b).

In the case of atoms of the boron type the total dipole forces

for ²S, ²P, ²D - ²P transitions have ratios of, on the average, 1:3.5:2 in the multi-configuration approximation as compared with 1:9:5 in the single-configuration approximation. The corresponding transition probabilities have ratios of, on the average, 1:1.9:0.16 as compared with 1:5:0.36 in the single-configuration approximation.

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Rec'd: 3 February 1953

BIBLIOGRAPHY

- Yutsis, A. P., ZhETF (J. Exp. Theor. Phys.), Vol. 19, 565, 1949.
- 2. Yutsis, A. P. and Kavetskis, V. I., ZhETF, Vol. 21, 1139, 1951.
- 3. Yutsis, A. P., ZhETF, Vol. 23, 129, 1952.
- 4. Morse, M., Young, L. A. and Haurwitz, E. S., Phys. Rev., 48, 948, 1935.
- 5. Fok, V. A. and Petrashen', M. I., ZhETF, Vol. 6, 1, 1936.
- 6. Veselov, M. G., ZhETF, Vol. 19, 959, 1949.
- 7. Moore, Ch. E., Atomic Energy Levels, Nat. Bur. Standards, Circ. 467, Washington, 1949.

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